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Liquid–Liquid Extraction of Vanadium(V) and Niobium(V) with Tris(2-ethylhexyl)phosphate: Mutual Separation of Vanadium(V), Niobium(V), and Tantalum(V), and Analysis of Steel Samples

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ABSTRACT

Tris(2-ethylhexyl)phosphate (TEHP) dissolved in toluene is used for selective extraction of vanadium(V) and niobium(V) from hydrochloric and hydrobromic acid solution. Vanadium is determined spectrophotometrically after backextraction from TEHP, whereas unstripped niobium is determined in the TEHP phase with thiocyanate. The probable extractable species is $VOCl_3 \cdot 2TEHP$ or $NbOCl_3 \cdot 2TEHP/NbOBr_3 \cdot 2TEHP$. The method permits mutual separation of vanadium(V), niobium(V), and tantalum(V), and provides analysis of vanadium and niobium in alloys with a high degree of accuracy and precision.

INTRODUCTION

Both vanadium and niobium are industrially important elements. Vanadium foil is used as a bonding material between steel and titanium sheets because it imparts tensile strength, toughness, and elasticity to the steel. Niobium, on the other hand, has potential value in electrolytic capacitors and promises to have an interesting future in the field of nuclear technology. In view of this, the separation and purification of vanadium and niobium are desired.

Very few solvent extraction methods that employ neutral extractants for vanadium(V), niobium(V), and tantalum(V) separation have been reported. The existing methods are critically reviewed in Table 1. These

TABLE 1
Critical Review of the Methods for the Solvent Extraction of Vanadium(V) and Niobium(V)

Metal ion	Extractant	Aqueous media	Special features	Ref.
V(V)	Isopropyl ether	Chloride	Separated from V(IV)	1
	Ethyl methyl ketone	Chloride	—	2
	Hexanol	Chloride	—	3
	3-Hydroxy-2-methylpyran-4-one	pH 1	Multiple extraction	4
	Tributyl phosphate	Chloride	Separation from Fe(II)	5–7
		Chloride	Extraction period 15 min. $VOCl_3 \cdot 2TBP$ species	
		Perchlorate or thiocyanate	V(IV) extracted synergistic effect of antipyrine	
	Tributyl phosphine oxide	pH 4	Synergistic effect of dithiozone and extraction period 10 min	
	Mesityl oxide	Chloride	Large interference	9
	Triisoamyl phosphate	Chloride	Needs salting out agent	10
Nb(V)	Bis (2-chloroethyl) ether	pH 4.1	—	11
	Ethyl methyl ketone	Fluoride and chloride	—	12
	Diisopropyl ketone	Chloride	Only 60% extraction	13
	Dioctyl hydrogen phosphate	Nitrate and fluoride	Zr(IV) coextract	14
	Dibutyl phosphate	Sulfate and peroxide	Extracted species $NbO(OH)_2(H_2O) \cdot TBP$	15
	Tributyl phosphate	Chloride	Extraction period 5 min and large interference	16, 17
		Sulfate	Distribution coefficient decrease at higher concentration of Nb	

methods suffer from such limitations as critical pH (4, 8, 11), multiple extraction (4), use of salting out agent (10), interference (9, 16), longer extraction period (8, 16), and incomplete extraction (13). In addition, mutual separation of vanadium(V), niobium(V), and tantalum(V) using a liquid–liquid extraction technique is lacking. This paper explores the potentialities of tris(2-ethylhexyl)phosphate (TEHP) as an extractant for the separation of vanadium(V), niobium(V), and tantalum(V).

EXPERIMENTAL

Apparatus

Absorbance and pH measurements were taken on a Spectronic 20-D (Milton Roy and Co) and a Control Dynamics digital pH meter with a combined glass electrode.

Reagents and Chemicals

The stock solution of vanadium(V) was prepared by dissolving 0.28 g ammonium metavanadate in 3 mL concentrated hydrochloric acid and diluting to 250 mL with distilled water. The solution was standardized titrimetrically (18). The stock solution of niobium(V) was prepared by fusing 0.071 g niobium pentoxide (Koch-Light) with 3 g potassium pyrosulfate. The resulting cooled melt was dissolved in 1 M tartaric acid and diluted to 100 mL with the same solution. For standard tantalum(V) solution, 2.5 g tantalum pentoxide (Koch-Light) was fused with potassium carbonate and potassium nitrate in the weight ratio 2:5:5. The cooled melt was dissolved in concentrated sulfuric acid. The acid was evaporated to almost dryness, and the residue was dissolved in 20% tartaric acid and diluted to 100 mL with distilled water. Niobium and tantalum solutions were standardized with *N*-benzoyl-*N*-phenylhydroxylamine (18).

Fluka grade TEHP dissolved in toluene was used for extraction and separation studies.

All other chemicals used were of analytical reagent grade.

General Extraction Procedure for Vanadium(V) and Niobium(V)

A 10-mL aliquot of solution containing microgram amounts of vanadium(V) and niobium(V) was extracted from halide media with TEHP in toluene under the optimum extraction conditions described in Table 2. After stripping, vanadium(V) in the aqueous phase was estimated spectrophotometrically with 4-(2-pyridylazo)resorcinol (PAR) by adding 0.5 mL of 1×10^{-1} M PAR, adjusting the pH to 5.5 (with dilute hydrochloric or sodium hydroxide), and measuring the absorbance of the red vanadium–PAR complex at 545 nm against the reagent blank prepared analogously (19). Niobium(V) in TEHP was determined spectrophotometrically

TABLE 2
Optimum Extraction Conditions for Vanadium(V) and Niobium(V)

Metal ion (μg)	Aqueous phase	Organic phase	Extraction period (s)	Stripping agent	Determination procedure
V(V) 10–30	5–6 M HCl	5 mL of 70% TEHP in toluene	90	2 × 5 mL water	Spectrophotometrically with PAR (19)
Nb(V) 5–30	6–7 M HCl or 5–5.5 M HBr	5 mL of 60% TEHP in toluene	60	—	Spectrophotometrically with thiocyanate in TEHP phase (18)

with thiocyanate by adding 2 mL of 15% tin(II) chloride solution, 5 mL of 9 M hydrochloric acid, and 1 mL of 1 M tartaric acid solution (freshly prepared). Dry the organic phase with anhydrous sodium sulfate and measure the absorbance of the yellow-colored niobium complex at 430 nm against the reagent blank prepared analogously (18).

RESULTS AND DISCUSSION

Extraction Condition

Variations in hydrochloric and hydrobromic acid concentrations of 1–7 M and a TEHP concentration of 30–70% using toluene as the diluent showed that the quantitative extraction of vanadium(V) occurs from 5–6 M hydrochloric acid solution with 70% TEHP in toluene (Figs. 1 and 2). Vanadium(V) shows no extraction from hydrobromic acid solution; niobium(V), however, extracts quantitatively from 6–7 M hydrochloric acid or 5–5.5 M hydrobromic acid with 60% TEHP. Tantalum(V) does not extract into TEHP either from hydrochloric or hydrobromic acid solution.

Effect of Diluents

The suitability of several diluents, such as benzene, toluene, xylene, hexane, cyclohexane, carbon tetrachloride, and chloroform, for the extraction of vanadium(V) and niobium(V) using the proposed method was investigated. It was found that TEHP dissolved in toluene or xylene showed quantitative extraction of vanadium(V) and niobium(V). In other diluents, extraction was incomplete.

Period of Extraction

The period of equilibration was varied from 30 to 180 seconds. The quantitative extraction of vanadium(V) and niobium(V) was feasible for 90 and 60 seconds, respectively. Prolonged shaking, however, had no adverse effect on the extraction of metal ions. Compared to other neutral organophosphorus compounds and even to other oxygenated solvents, TEHP facilitates faster extraction and separation.

Nature of Extracted Species

The nature of extracted species was deduced from log *D*–log *C* plots. A plot of log of distribution ratio vs log of TEHP concentration at 6.0 M hydrochloric acid gave slopes of 2.34 and 2.19 for vanadium(V) and niobium(V), respectively (Fig. 3). Similarly, a plot of log of distribution ratio vs log of hydrochloric acid concentration at 70% TEHP gave a slope

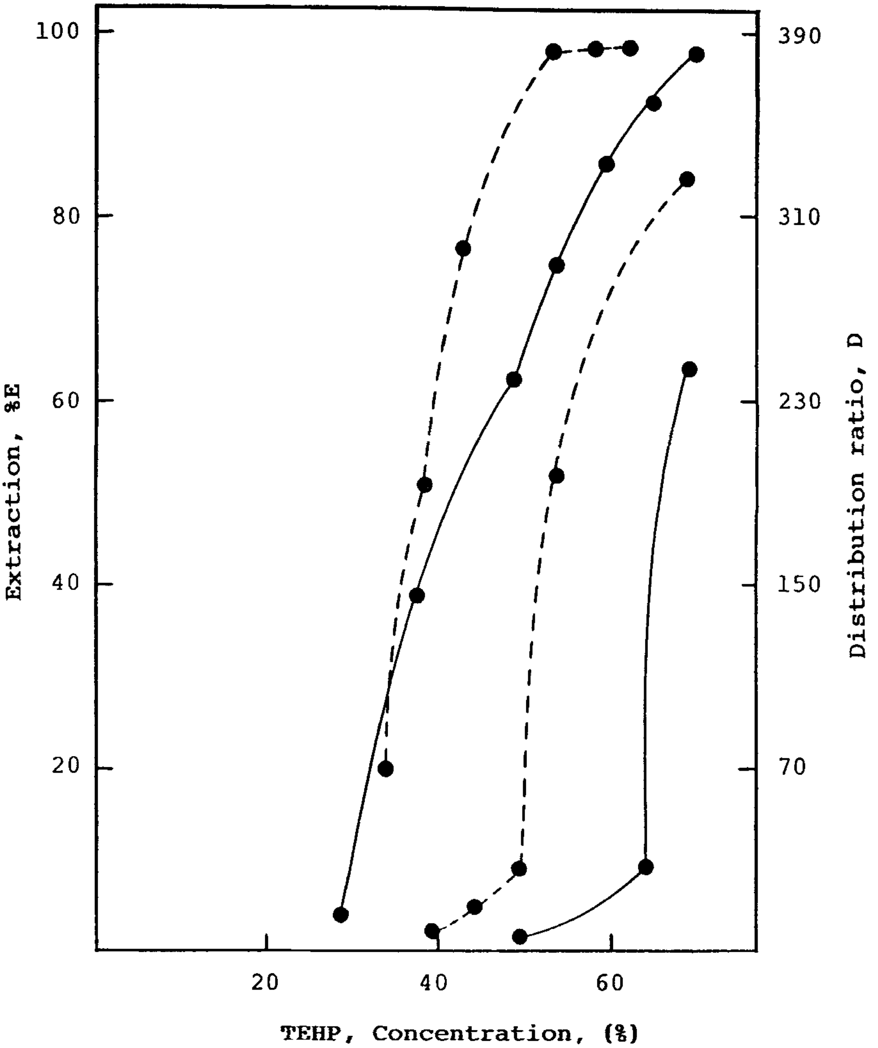


FIG. 1 Extraction behavior of vanadium(V) (———) and niobium(V) (----) as a function of TEHP concentration at 5 and 6 M hydrochloric acid, respectively.

of 3.15 for vanadium(V). For niobium(V), log of distribution ratio vs log of hydrochloric acid concentration or log of hydrobromic acid concentration at 60% TEHP gave slopes of 3.00 and 3.30, respectively (Fig. 4). This indicates there is a metal-to-halide ratio of 1 : 3 and a metal-to-TEHP ratio

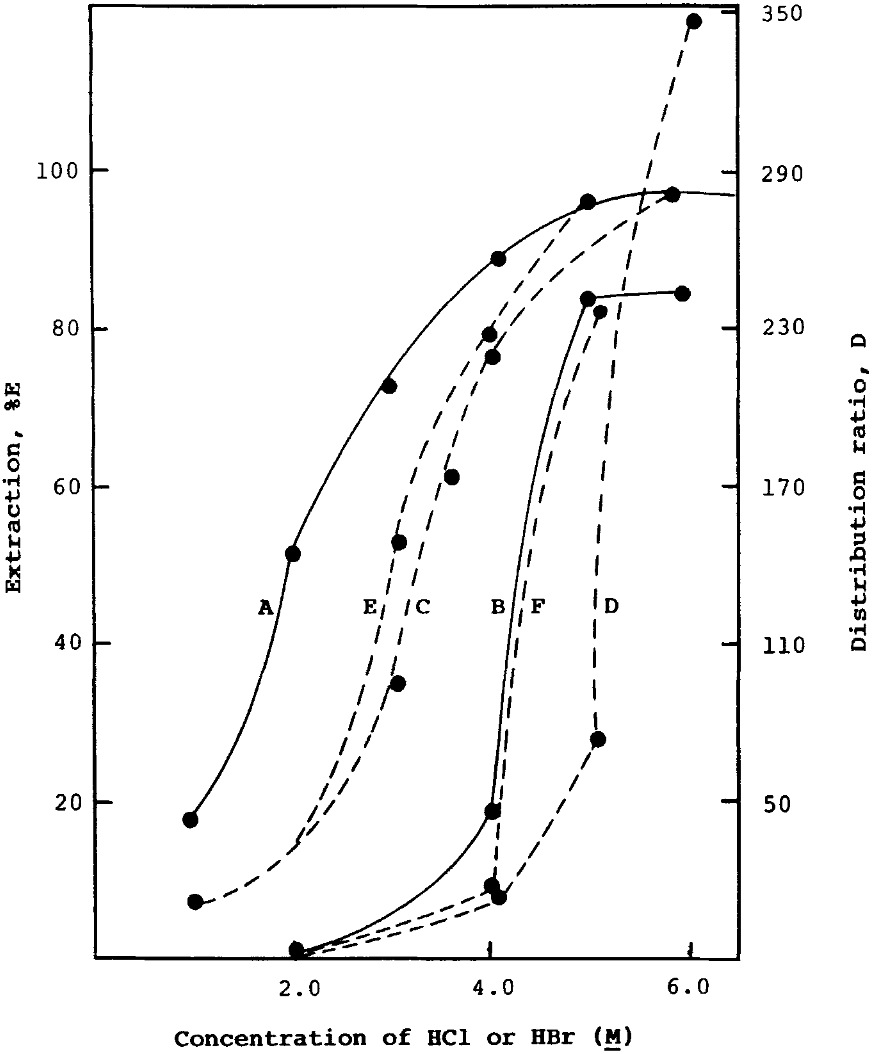


FIG. 2 Extraction behavior of vanadium(V) (——) and niobium(V) (----) as a function of hydrochloric and hydrobromic acid concentration at 70 and 60% TEHP in toluene. Curves A and B: For vanadium(V) from hydrochloric acid. Curves C and D: For niobium(V) from hydrochloric acid. Curves E and F: For niobium(V) from hydrobromic acid.

of 1:2 in the extractable species. Hence, the probable extracted species is $MOX_3 \cdot 2TEHP$ where M is either vanadium or niobium, X stands for Cl^- or Br^-, and TEHP is the extractant. The extraction mechanism involves solvation of oxo salts by TEHP. Thus,

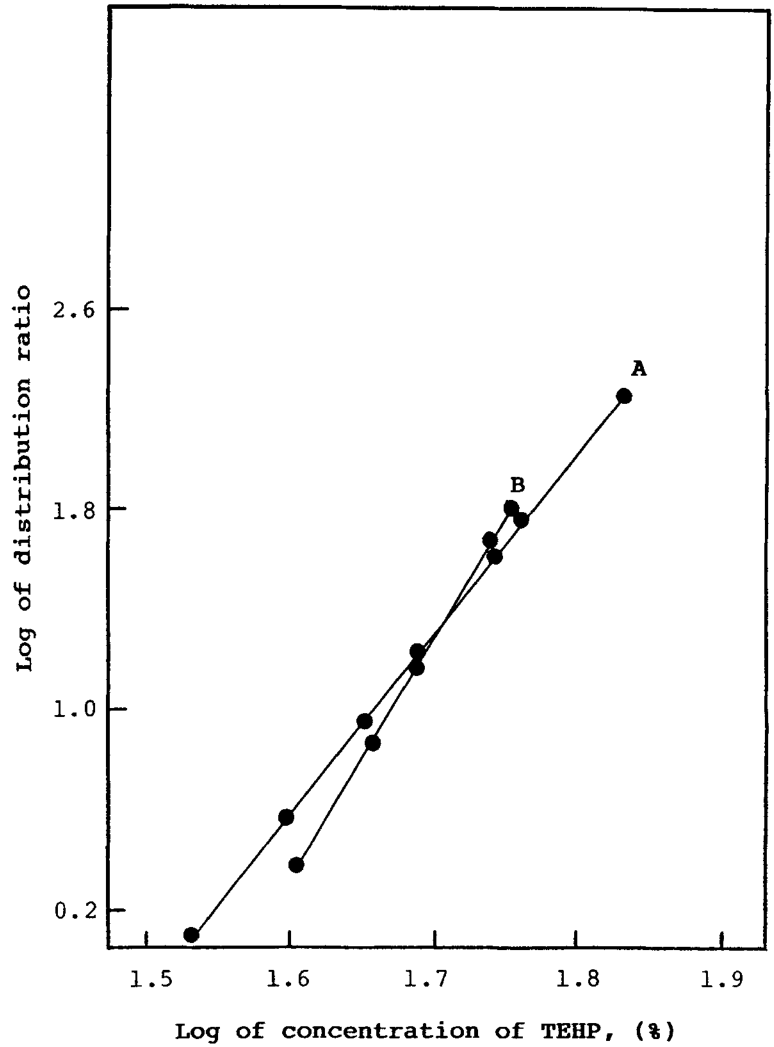


FIG. 3 A: Plot for vanadium(V) at 5 M HCl. B: Plot for niobium(V) at 6 M HCl.

$$MOX_3 \cdot 2H_2O + 2TEHP \rightleftharpoons MOX_3 \cdot 2TEHP + 2H_2O$$

where $MOX_3 \cdot 2TEHP$ is the solvated oxo salt of vanadium or niobium.

TEHP contains the phosphoryl group P=O; this group is the principal cause for solvation of the oxo salt which renders them hydrophobic and favors extraction. Disolvated MOX_3 species have been investigated by earlier workers (6).

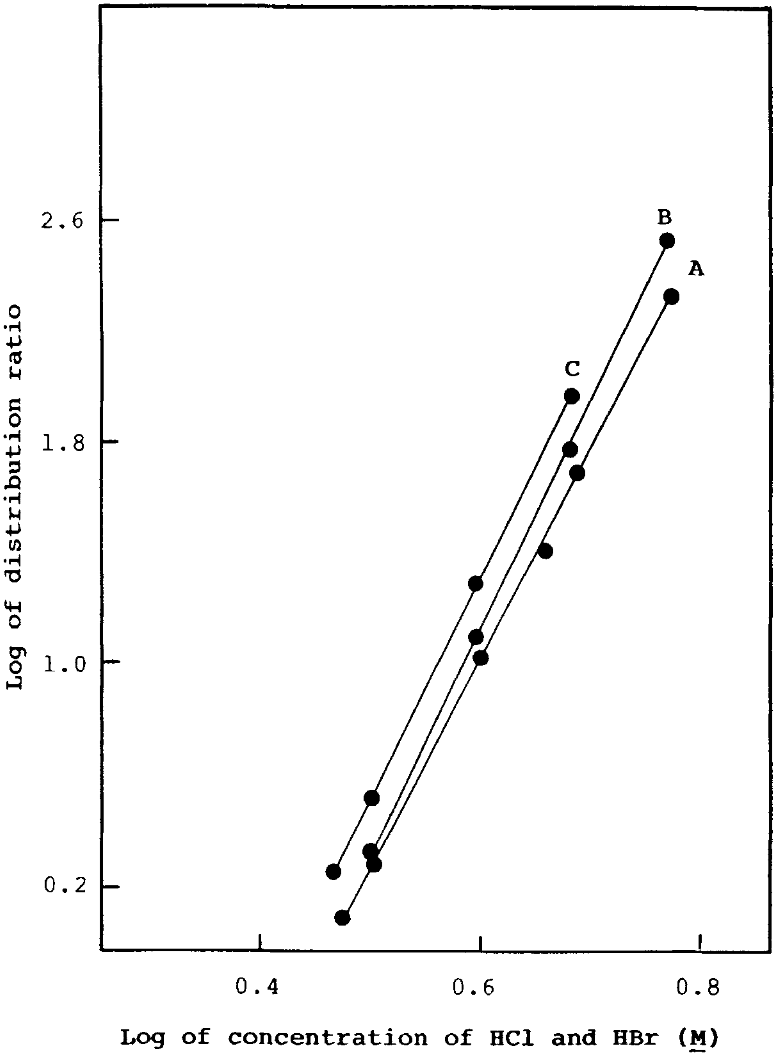


FIG. 4 A: Plot for vanadium(V) at 70% TEHP. B and C: Plot for niobium(V) for hydrochloric and hydrobromic acids, respectively, at 60% TEHP.

Effect of Foreign Ions

Varying amount of foreign ions were added to a fixed amount of vanadium(V) (20 μg) and niobium(V) (10 μg) to study their interference. The tolerance limit was set at the amount required to cause ±1% error in metal recovery. The results are reported in Table 3.

TABLE 3
Effect of Foreign Ions on the Extraction and Determination of Vanadium(V)[a] and Niobium(V)[b]

	Tolerance limit (μg)			Tolerance limit (μg)	
Ions	Vanadium(V)	Niobium(V)	Ions	Vanadium(V)	Niobium(V)
Ag(I)	1000	500	Al(III)	4500	3500
Ba(II)	3000	2000	Ru(III)	500	200
Mg(II)	5000	1500	Fe(III)[c]	50	100
Cd(II)	2000	2500	Pt(IV)	3500	2000
Ni(II)	3000	2500	Zr(IV)	2500	3500
Cu(II)	None	None	Se(IV)	350	150
Pb(II)	450	350	W(VI)	500	200
Sn(II)	1500	1000	Mo(VI)	None	50
Be(II)	2000	1500	Cr(VI)	200	100
Hg(II)	500	400	Citrate	4000	2000
Zn(II)	3000	3500	Tartrate	5500	3500
Bi(III)	1500	1000	EDTA	2500	1000
In(III)	None	50	Oxalate	2000	1500
Tl(III)	500	200	Phosphate	3000	3000
Ga(III)	800	1500	Thiourea	800	300
Os(III)	1000	800	Thiosulfate	2000	1000

[a] Vanadium(V) (20 μg): Aqueous phase = 5 M HCl, organic phase = 5 mL of 70% TEHP in toluene.

[b] Niobium(V) (10 μg): Aqueous phase = 6 M HCl, organic phase = 5 mL of 60% TEHP in toluene.

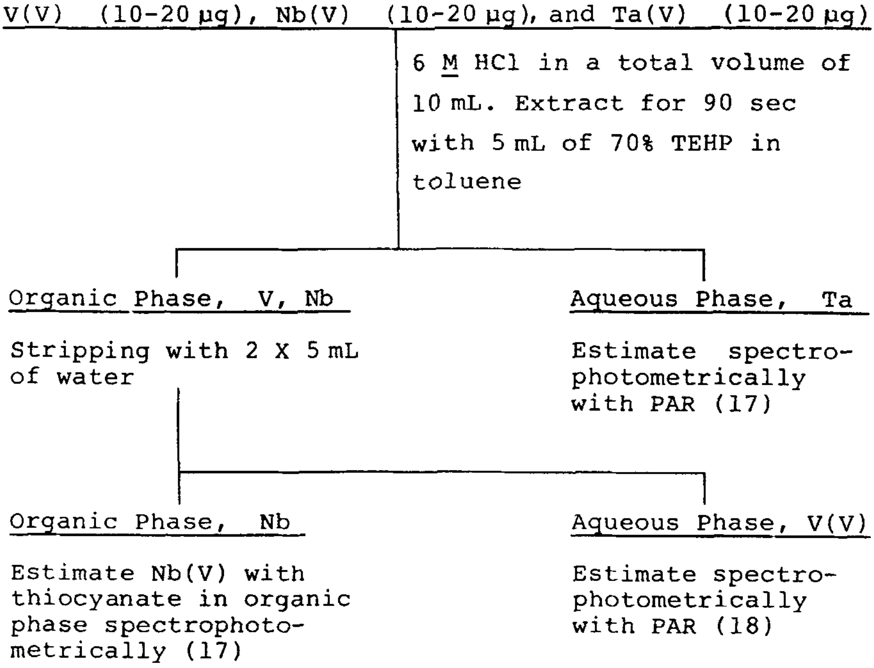
[c] Iron(III) is masked with 600 μg EDTA.

Mutual Separation of Vanadium(V), Niobium(V), and Tantalum(V)

Vanadium(V), niobium(V), and tantalum(V) were separated from a ternary mixture by the scheme shown in Fig. 5. The recoveries of vanadium(V), niobium(V) and tantalum(V) were ≥ 99.0% (Table 4).

Application to the Analysis of Alloys

The proposed method was applied to the separation and determination of vanadium and niobium in alloys such as electric welding alloy and a standard aluminum alloy (BCS 195). Fifty milligrams of electric welding alloy was dissolved in 10 mL hydrofluoric acid, evaporated almost to dryness, and the residue taken up in water. After filtering off the residue, the filtrate was diluted to 100 mL. A 1-mL aliquot containing 15 μg niobium was taken for extraction, separation, and determination by the pro-



V(V) (10-20 µg), Nb(V) (10-20 µg), and Ta(V) (10-20 µg)

6 M HCl in a total volume of 10 mL. Extract for 90 sec with 5 mL of 70% TEHP in toluene

Organic Phase, V, Nb

Stripping with 2 X 5 mL of water

Aqueous Phase, Ta

Estimate spectrophotometrically with PAR (17)

Organic Phase, Nb

Estimate Nb(V) with thiocyanate in organic phase spectrophotometrically (17)

Aqueous Phase, V(V)

Estimate spectrophotometrically with PAR (18)

FIG. 5 Scheme for the mutual separation of vanadium(V), niobium(V), and tantalum(V) in ternary mixture.

TABLE 4
Analysis of Synthetic Mixtures

Analysis	Mixture (µg)	Recovery[a] (%)	Standard deviation	Coefficient variation (%)
1	V, 20	V, 99.2	V, 0.74×10^{-3}	V, 0.24
	Nb, 10	Nb, 99.4	Nb, 0.63×10^{-3}	Nb, 0.36
	Ta, 20	Ta, 99.6	Ta, 0.57×10^{-3}	Ta, 0.20
2	V, 10	V, 99.4	V, 0.57×10^{-3}	V, 0.18
	Nb, 20	Nb, 99.2	Nb, 0.63×10^{-3}	Nb, 0.17
	Ta, 10	Ta, 99.7	Ta, 0.89×10^{-3}	Ta, 0.16
3	V, 10	V, 99.1	V, 0.99×10^{-3}	V, 0.32
	Nb, 10	Nb, 99.6	Nb, 0.42×10^{-3}	Nb, 0.11
	Ta, 20	Ta, 99.5	Ta, 0.57×10^{-3}	Ta, 0.20

[a] Average of six determinations.

TABLE 5
Application to the Analysis of Alloys

Alloy	Composition (%)	Certified value (%)	V/Nb found[a] (%)	Standard deviation	Coefficient variation (%)
Electric welding alloy	C, 0.67 S, 0.008 P, 0.002 Si, 0.919 Nb, 3.0 Pb, 0.29 Bi, 0.05 Ti, 0.05	Nb, 3.0	2.99	0.2×10^{-3}	0.42
Standard aluminum sample BCS 195[b]	Al, 99.5 SiO_2, 0.003 Fe, 0.08 Cu, 0.001 Mn, 0.001 Ti, 0.002 Zn, 0.015 V, 0.004 Ga, 0.009	V, 0.004	0.0039	0.8×10^{-3}	0.90

[a] Average of six determinations.
[b] British Chemical Standards.

posed method. A standard aluminum alloy (BCS 195) weighing 12.5 g was dissolved in 5 mL aqua regia and diluted to 25 mL. A 1-mL aliquot containing 20 μg vanadium, 600 μg iron, and 5 μg copper was taken for extraction and determination study by the proposed method. Since iron and copper interfere in the estimation of vanadium, they were masked with 600 μg EDTA. The results of the analysis are reported in Table 5. The total time required for the analysis was 20 minutes.

CONCLUSION

The highlights of the proposed methods are:

1. Provides mutual separation of vanadium(V), niobium(V), and tantalum(V).
2. The method is applicable to alloy steels.
3. The method is free from interference.
4. Extraction time is short.
5. The method is reproducible.

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